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**PRESSURE INDUCED RESONANCE RAMAN EFFECT IN
SHOCKED CARBON DISULFIDE**

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ABSTRACT

Time-resolved Raman spectroscopy to study shock-induced processes in condensed materials has been developed and used to examine solid carbon disulfide subjected to stepwise shock wave loading to a peak pressure of 8 GPa. Pressure shifts of the symmetric stretching mode, ν_1 and the first overtone of the bending mode, $2\nu_2$ have been measured, and the separation between the two bands is observed to decrease with pressure. These results are in agreement with the static high pressure measurements. Enhancement of the Raman cross section of carbon disulfide is observed at pressures higher than 7 GPa and can be understood in terms of a pressure induced resonance Raman effect.

Understanding shock induced chemical processes in condensed materials requires knowledge about the molecular structure, chemical species and kinetics in these experiments. Hence, spectroscopic techniques have been used increasingly in recent years [1,2] to complement the bulk or continuum measurements [3] that are normally obtained in shock wave experiments. A good review of the spectroscopic methods used in shock compression experiments including difficulties associated with such measurements has been presented by Moore and Schmidt [4].

Raman spectroscopy is a useful method to study chemical processes under high pressures because it measures changes in both inter- and intra- molecular forces and the measurements can be related to structure, compressibility, and temperature. Various Raman techniques have been developed for many different applications at ambient conditions [5,6]. CARS [7] and spontaneous Raman [8] measurements have been reported under shock loading. Use of spontaneous Raman spectroscopy in shock studies is attractive because it is experimentally simpler and the results are easier to interpret. However, it has not been widely used because of small scattering cross sections and difficulties due to large temperature rise that can cause band broadening and large background due to emission. Here we describe a method to obtain time-resolved Raman measurements in shocked carbon disulfide. The ability to make time-resolved measurements is expected to be particularly important for chemical reaction studies in shocked materials.

Carbon disulfide is a typical example of a material which undergoes shock induced irreversible chemical changes that are accompanied by drastic electronic changes [9]. Several studies have been carried out to understand shock induced chemical reaction in CS₂ using both continuum [10,11] and time-resolved spectroscopic measurement techniques [12,13]. However, a detailed understanding has not yet been achieved, mainly due to the uncertainty regarding structure and chemical species in the shocked state. Carbon disulfide is a linear molecule that crystallizes



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at 173 K to an orthorhombic structure with a space group $D_{2h}^{18}(C_{mca})$ having two molecules per primitive unit cell which occupy sites of C_{2h} symmetry [14]. Vibrational modes of solid carbon disulfide including normal modes (ν_1, ν_2, ν_3), translational lattice modes (B_{1u}, B_{2u}), and rotational lattice modes (A_g, B_{1g}, B_{2g} , and B_{3g}), have been previously studied at cryogenic temperatures under both ambient pressure [15] and static high pressure [16,17]. In this report we describe shock induced changes on the symmetric stretching mode, ν_1 , and first overtone of the bending mode, $2\nu_2$, and their intensities.

The overall experimental arrangement is shown in Fig. 1. Details related to sample assembly and impact experiment procedures can be seen elsewhere [18]. A carbon disulfide sample, approximately 0.1 mm thick, is contained between two z-cut sapphire (Union Carbide Co.) windows. Temperature of the sample is lowered by circulating liquid nitrogen and is measured using a Chromel-Alumel thermocouple. A third sapphire disc, used as an impactor, is mounted on an aluminum projectile and accelerated using a light gas gun [19] to the desired velocity. Upon impact a shock wave is produced in the impacting discs. The pressure and temperature of the sample increases in a stepwise manner, due to the difference of shock impedences between the sapphire and carbon disulfide [18]. These pressure changes are calculated using the Rankine-Hugoniot jump conditions in combination with a nonlinear elastic equation of state for sapphire [20] and an equation of state for carbon disulfide [21].

A Xe-flashlamp pumped dye laser (Candella, Model SLL-500) furnished with a prism-tuning wavelength selector, is used as a light source. The 514.5 nm line selected from the Coumarin fluorescence was used for excitation. The beam has a relatively large diameter, 10 mm, and divergence, 1 mrad. Therefore, an iris is used to select an appropriate beam diameter, typically less than 3 mm. The beam is

focused on the sample at near 20 degree from the axis of the sample cell. In this configuration the reflection from the aluminum projectile surface can be filtered by an iris mounted at the back of the sapphire impactor, and the additional reflections from the interfaces among sapphire window, sample, and air can be spatially eliminated. Raman signal from the sample is collected and focused at the 0.25 m double grating spectrograph using two matching lenses. An edge filter is used to minimize the elastically scattered light from the Raman scattered light. The spectrograph output is imaged at the electronic streak camera (Imacon model 790) for temporal dispersion. The streak camera output is intensified using a fiber optically coupled micro-channel plate intensifier and is recorded on an intensified Vidicon detector. An optical multichannel analyzer is used to read the data. Typical resolution of the system is approximately 30 nsec in time and 0.5 Å in wavelength. Calibration of the wavelength was done using Raman lines from a standard material and/or the Rayleigh scattering line. Both measurements showed good agreement within the resolution of the system. Further details about the detection system can be found elsewhere [22].

Intensity and time-profile of the laser output is quite reproducible over a number of flash lamp firings. Intensity of the laser increases rapidly to the peak value within 300 nsec, and monotonically decreases to zero for the next 1 μ sec; the full width at half maximum (FWHM) is approximately 600 nsec. To avoid stimulated Raman signal [23], the minimum laser energy (10 mJ) needed to obtain a reasonable spontaneous Raman signal was used.

Fig. 2 shows typical time-resolved spontaneous Raman spectra of the solid carbon disulfide in a region of 400 and 900 cm^{-1} , at ambient pressure and 162 K. The spectra shown were obtained at 30 nsec intervals. The peak corresponding to the symmetric stretching mode (ν_1) of CS_2 is most easily seen in approximately the first 20 tracks (600 nsec). The normalized intensity of the ν_1 peak with respect to

the incident laser intensity remains nearly constant for all the tracks. This implies that the signal in Fig. 2 is due to the spontaneous Raman process.

The Raman spectrum from solid CS₂, at 160 K, is substantially altered under shock compression, as illustrated in Fig. 3. Comparing Figures 2 and 3 we see that signal intensity is significantly enhanced in the latter tracks. In these later tracks, the signal persists even as the output of the laser is decreasing substantially.

The calculated pressure (Top) and Raman intensities for ν_1 normalized by the incident laser intensity (Bottom) are illustrated as a function of time in Fig. 4. The circles and triangles represent the normalized intensities of the unshocked and shocked carbon disulfide, respectively. Time zero indicates the time of impact. The symbols (a) through (d) indicate times for the different events: shock enters the sample (a), sample pressures reach 7 GPa (b) and the final value 8 GPa (c), and the rarefaction wave enters the cell (d). As expected, the Raman signal of the unshocked carbon disulfide follows the laser profile. Similar behavior is noticed in the Raman spectra of the shocked carbon disulfide at pressures less than 7 GPa. At higher pressures, the normalized intensity increases continuously until the rarefaction wave, originating at the back of the sample cell, lowers the sample pressure. The highest value in the normalized intensity in Figure 4 is not coincident with the calculated pressure profile just prior to the pressure decrease. This difference is most likely due to an uncertainty in temporal correlation between the calculated profile and the OMA record because of 1-2 track uncertainty in the OMA results.

Typical Raman spectra of the unshocked and shocked carbon disulfide (at 8 GPa) are illustrated in Fig. 5. The peak at 654 cm⁻¹ is the symmetric stretching vibration of the carbon disulfide and the shoulder near 635 cm⁻¹ is that of the carbon disulfide isotope. Although first overtones of the bending mode, $2\nu_2$ centered at 786 and 802 cm⁻¹ are not clear at ambient conditions due to the poor signal-to-noise ratio, both their intensities and positions are reproducible from shot to shot.

More importantly, these features become distinctive at higher pressures.

Two changes are noteworthy in Fig. 5. The intensities of both ν_1 and $2\nu_2$ peaks are increased, and the separation between the two bands is decreased as the sample pressure is increased; the ν_1 peak shifts towards the higher frequency by 6 cm^{-1} , whereas the $2\nu_2$ shifts towards the lower frequency by approximately 7 cm^{-1} . These pressure shifts under shock loading agree with the previous Raman measurements under static conditions [16].

The most interesting result here is the enhancement of the Raman lines at pressures higher than 7 GPa. This can be understood in terms of a pressure induced resonance Raman effect. A simplified picture representing possible Raman processes in the shocked carbon disulfide is shown in Fig. 6. It has been previously observed that shocked carbon disulfide shows a strong shift of the electronic transition towards the red [9,18]. For example, at ambient pressure the absorption band edge is located at approximately 360 nm, whereas at 8 GPa it moves to near 510 nm. At ambient pressure the excitation line, 514.5 nm, is well separated from the excited states as shown in Fig. 6(a) and the Raman process is initiated from a "virtual" state. However, at 8 GPa the excited electronic level is shifted to near the frequency of incident light as shown in Fig. 6(b), and the Raman processes is then initiated from an "active virtual" state which can resonate with the excited electronic state. At the condition (a), the intensity of the Raman lines are proportional to $(\nu_o - \nu_i)^4 = \nu_o^4$ [24], where ν_o is the exciting frequency and ν_i is the Raman shift of the i^{th} fundamental mode. At near resonance condition (b), the Raman intensity of the symmetric mode is proportional to $(\nu_o - \nu_i)^4 * [(\nu_e^2 + \nu_o^2)^2 / (\nu_e^2 - \nu_o^2)^4]$ [25-27], where ν_o is the exciting frequency, ν_i is the Raman shift of the i^{th} fundamental mode, and ν_e is the frequency of the electronic excited state. As the pressure shifts the frequency ν_e of the carbon disulfide towards ν_o , the intensity of the Raman spectra is expected to increase. Based on the edge shifts of the

absorption band [18], the Raman intensity is expected to increase by a factor of 5 between 7 and 8 GPa, which is consistent with the observation.

It is also interesting to note that the Raman signal continues to increase even after the pressure in the sample reaches its maximum value. This suggests that either the relaxation time of the transition is long or, more likely, that the absorption cross section, which has a linear relation with the Raman cross section near the resonance condition, is increasing with time. In preliminary absorption measurements, we have observed that the absorption cross section of pure carbon disulfide is increased by nearly a factor of 2 at 4 GPa, for a 100-200 nsec time period.

Because the solid carbon disulfide occupies two different sites of the unit cell, the doubly degenerate ν_2 band in the liquid is split into two different bands in the solid, as seen in Fig. 5. This splitting persists at the maximum pressure, 8 GPa, and suggests that the carbon disulfide remains a solid in the shocked state. The calculated temperature of the carbon disulfide at 8 GPa is approximately 260 K and this would also suggest that the carbon disulfide is in the solid phase based on the phase diagram of CS₂ obtained in static experiments [28].

The pressure shift of $2\nu_2$ is different from that of ν_1 , and the separation between two bands decreases. Similar behavior has been previously observed in carbon disulfide [16] and carbon dioxide [29] under static pressure conditions, and it has been explained in terms of weakening of the Fermi resonance interaction.

In summary, time-resolved Raman spectroscopy to study shock-induced processes in condensed material has been developed and its feasibility has been shown by measurements in solid carbon disulfide. Enhancement of the Raman cross section of the solid carbon disulfide has been observed at pressures higher than 7 GPa and has been explained in terms of the pressure induced resonance Raman effect. Pressure shifts of the symmetric stretching and the first overtone of the bending mode have been measured and are in agreement with static experiments

[16]. Although the present work represents a start, the pressure induced resonance effect is expected to be useful in shock wave studies of chemical and physical processes because of intensity enhancement and the potential for monitoring "local" vibrational motions. Further work on this problem is currently underway.

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FIGURE CAPTIONS

- Fig. 1. Experimental arrangement for time-resolved Raman measurement. The thickness of the sample represented by the shaded region has been exaggerated in the figure for clarity. The symbols in the figure are defined as follows: P for Photodiode, I for iris, L for lens, M for mirror, and F for filter
- Fig. 2. Time-resolved Raman spectrum of solid carbon disulfide at ambient pressure and 162 K. Each spectrum is collected for 30 nsec and the peak represents the spontaneous Raman signal of the symmetric stretching mode of carbon disulfide.
- Fig. 3. Time-resolved Raman spectrum of carbon disulfide shocked to 8 GPa at 160 K. Each spectrum is collected for 30 nsec and the peak represents the spontaneous or resonance enhanced Raman signal of the symmetric stretching mode of carbon disulfide.
- Fig. 4. The calculated pressure and normalized intensity of the symmetric stretching mode as a function of time. Circles and triangles are the values for the unshocked and shocked carbon disulfide, respectively. Time zero indicates the time of impact. (a). time of shock entering the cell. (b). pressure of the sample reaches 7 GPa. (c) pressure reaches the peak value of 8 GPa, and (d) rarefaction wave arrives at the cell.
- Fig. 5. Raman spectra of solid carbon disulfide in the regions between 400 and 900 cm^{-1} , at ambient pressure (Bottom) and 8 GPa (Top).
- Fig. 6. Simplified picture of Raman processes showing pressure induced resonance Raman effect under shock compression. (a). Spontaneous Raman process at ambient pressure, (b) pre-resonance Raman process at 8 GPa. Numbers are based on the pressure shifts measured previously in Ref 18.

The intent of this figure is to merely point out the decrease in the separation between the ground and excited state. The exact nature of the excited state potential is not known.











